Research Article

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Synthesis and Characterization of Pure and Copper Doped ZnO Nanoparticles

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ABSTRACT

The evolving concept in the field of science and technology is nanotechnology. In this present work, the zinc oxide nanoparticles (ZnO) were successfully synthesized using both biological and chemical techniques. Pure and Cu doped Zinc oxide particles were prepared by co-precipitation method associated with microwave irradiation method. The prepared Cu doped ZnO were characterized by XRD, SEM, EDAX and UV techniques. The X-ray diffraction (XRD) pattern analyses reveal the crystalline size of the nanoparticles. The morphology and purity of the sample were analyzed by scanning electron microscopy (SEM) and Energy Dispersion X-ray Diffraction (EDAX) analysis. The optical properties carried out by Ultra-Violet spectroscopy (UV). The results are matches well with standard values.

Keywords: Pure Zinc Oxide; Copper doped Zinc; Crystalline size; Morphology; Optical properties.

1. INTRODUCTION

Nanotechnology is the recent advanced technology. It mainly focuses on the synthesis of nanoparticles of various sizes, shapes, and compositions involved in several applications. Zinc Oxide nanoparticle is one of the most popular metal oxide nanoparticles. Nanomaterials are believed to be next-generation molecules with huge potential in diverse fields, including medicine, catalysis, sensors, and so forth. ZnO is considered one of the most important oxide materials due to its unique features and wide range of technologically important applications.

ZnO is an n-type semiconductor. Moreover, it is cheap and environmentally friendly as compared to other metal oxides. Due to these properties have found potential applications in fields such as gas sensors, solar cells, varistors, light-emitting devices, photocatalyst, antibacterial activity, and cancer treatment. ZnO lacks a centre of symmetry, making it beneficial for its use in actuators and piezo electronic transducers. Several methods have been devoted to the fabrication of transition metal-doped ZnO nanoparticles, the co-precipitation method. Among these methods, the co-precipitation method is of great interest because of its simplicity, low equipment cost, relatively lower processing temperature, and environmentally benign. This method is advantageous over other methods because the reagents are mixed at the molecular level, and therefore, there is good control of stoichiometry, morphology, purity and homogeneity.

Properties of ZnO can be tuned according to the research interest by doping with various metal atoms to suit specific needs and applications. Metal doping induces drastic changes in the optical, electrical and magnetic properties of ZnO by altering its electronic structure. Many authors have reported the changes induced by the incorporation of transition metal ions into ZnO lattice. Albeit a large number of reports on transition metal-doped ZnO system, very less work is done on Cu doped ZnO. Substitution of copper into the ZnO lattice has improved properties such as photocatalytic activity, gas sensitivity and magnetic semiconductivity. Copper doped zinc oxide was found to exhibit ferromagnetic performance at room temperature. Photoluminescence (PL) of Cu doped ZnO nanocrystals were found to show pronounced UV emission and negligible visible emission with peak positions coinciding with that of undoped ZnO. Literature shows the substitution limit of Cu in ZnO to be low (around 5 at%). So, this work is a strategy to synthesize a higher compositional level of copper doped ZnO lattice. The present investigation deals with the synthesis of Cu doped ZnO Nanopowders with Cu content varying from 5 to 30 at% via co-precipitation method, followed by the characterization of samples using Transmission Electron Microscopy (TEM), Powder X-ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR) techniques. The influence of Cu content on the structural and electrical properties has also been investigated (Singhal *et al.* 2012).

2. MATERIALS & METHODS

Zinc acetate dihydrate ($C_4H_{10}O_6Zn$) and Copper Sulphate ($CuSO_4$). Zinc Acetate Dihydrate is a moderately water-soluble crystalline Zinc source that decomposes to Zinc oxide on heating. Copper sulphate is an inorganic compound that combines sulphur with copper. Then the preparation, 4.9g of Zinc acetate dihydrate were taken in a beaker with 50 ml of distilled water. The solution was stirred for 30 minutes. Moreover, 0.6242g of $CuSO_4$ was taken in another beaker with 50ml of distilled water. This solution was stirred for 30 minutes. The $CuSO_4$ solution was added into Zinc acetate dihydrate solution. The both solutions were stirred for 30minutes. Then 5 g of Na $(OH)_2$ were taken and dissolved in 10ml of distilled water. This NaOH solution was added drop by drop into Cu doped ZnO solution. The pH reaches up to 12 until they reach. It allowed to stirred 45 minutes. And then, the prepared solution was aged for one day at room temperature. And then, the precipitates were washed with distilled water. Then the precipitate was dried for 35minutes in a domestic microwave oven at 70 watts. Finally, this nanopowder was grained by using mortar**.**

Pure ZnO powder preparation, 10.975 g of Zinc acetate dihydrate were taken in a beaker with 150 ml of distilled water. The solution was stirred for 30 minutes. Then 5g of Na $(OH)_2$ were taken and dissolved in 10ml of distilled water. This Na (OH) solution was added drop by drop into the Zinc acetate dihydrate solution. The pH reaches up to 12 until they reach. It allowed to stirred 30 minutes. And then, the prepared solution was aged for one day at room temperature. And then, the precipitates were washed with distilled water. Then the precipitate was dried for 45minutes in a microwave oven at 70 watts. Finally, this nanopowder was grained by using mortar**.**

3. CHARACTERIZATION TECHNIQUES

3.1 FTIR

This spectroscopy (FTIR) is an analytical technique used to identify the functional groups of prepared samples. The spectrum was recorded in the range of 4000-400 cm^{-1} region[10].

3.2 XRD

X-Ray diffraction (XRD) in a crystalline solid, the constituent particles (atoms, ions or molecules) are arranged in regular order. Interaction of a particular crystalline solid with X-rays helps in investigating its actual structure. Crystals are found to act as diffraction gratings for X-rays, and this indicates that the constituent particles in the crystals are arranged in planes at close distances in repeating patterns.

The lattice parameter calculated by the equation of

$$1/d2 = (4(h2+hk+K2)/3a2) + (l2/c2))$$

The crystalline size of the particle was defined from Debye -Scherrer's formula

$$D = k\lambda/\beta \cos \theta$$

Where, D-average crystalline size, K-broadening constant,

λ- wavelength of XRD, β- full width half maximum, θ-Bragg's angle.

3.3 EDAX & SEM

Energy dispersive spectroscopy is used to identify the elemental composition of the sample. The surface Morphologies of synthesised ZnO samples were analysed using Scanning Electron Microscopic analysis (SEM).

3.4 UV & PL

UV-Vis and photoluminescence spectroscopies are express the Optical properties of the samples.

4. RESULTS

4.1 FTIR Analysis

The Fourier transform infrared spectra of pure and Cu doped ZnO Nanoparticles are shown in fig 4.1. FTIR is used to investigate the functional elements in the synthesized nanoparticles. Fourier Transform Infrared Spectroscopy (FTIR) identifies chemical bonds in a molecule by producing an infrared absorption spectrum. The FTIR spectrum of the prepared pure and capped ZnO samples were plotted between the wavelength ranges about 4000-500 cm^{-1} is shown in fig 1. The verity of peaks is absorbed in the different wavenumbers. A large number of absorption peaks is 3733.72 cm^{-1} and 3882.70 cm^{-1} it corresponds to the O=H stretching banded. The peak at 2298.72 cm^{-1} and 2353.15 cm^{-1} it indicates the C=H bond. The absorbance at 2800 cm^{-1} and 2793.15 cm^{-1} ants it's represented the C=H bond. The absorption peaks at 1689.26 cm^{-1} and 1724.36 cm^{-1} it indicates the presence of H=O=H stretching. And then, C=HO stretching absorption represents the peak at 1153.69 cm^{-1} and 1170.79 cm^{-1}, respectively. Those results indicate that the synthesized ZnO nanoparticles are stabilized by Chemical molecular constituents present in the Copper doping particles is shown in Table 1.

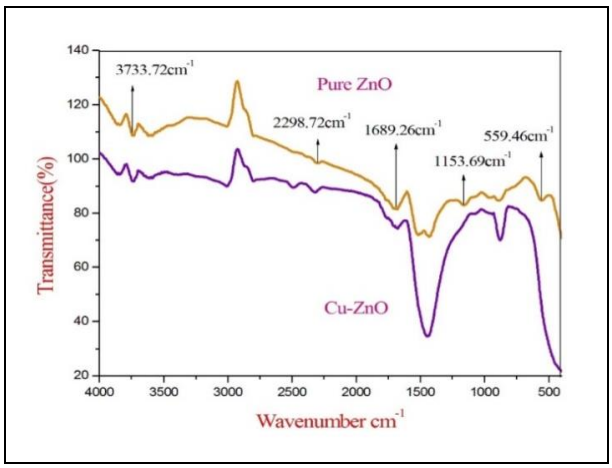

Fig. 1: FTIR Spectrum of Pure and Cu Doped ZnO

4.2 EDAX

Energy-dispersive X-ray spectroscopy (EDX) provides a qualitative and quantitative analysis. The chemical composition of the elements was determined by this technique. The EDX analysis of pure and Cu doped ZnO is shown in Fig 2 (a) & (b). The functional groups of Cu, Zn, and O are present in the sample. It confirms the purity of the composition elements (table 2).

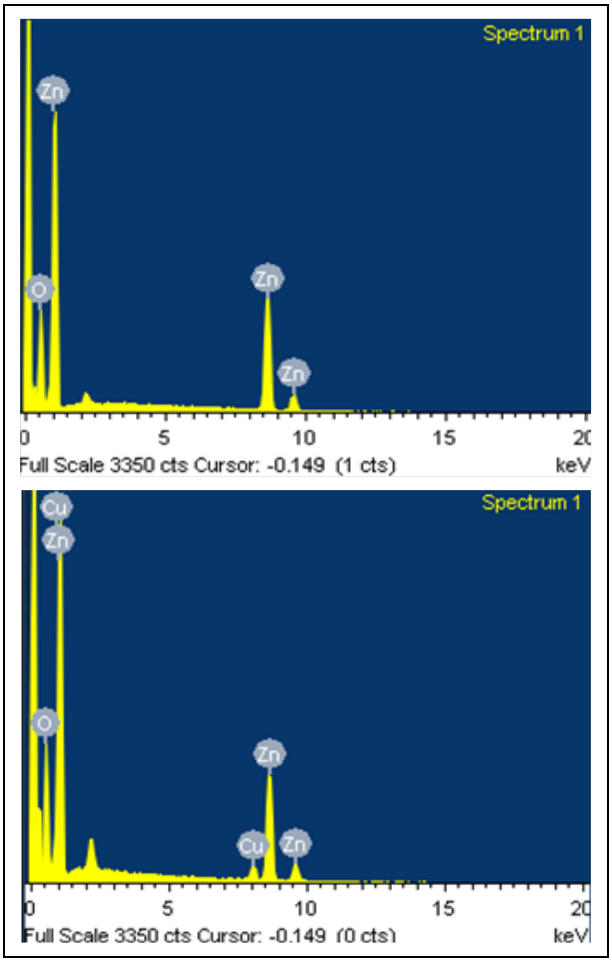

Fig. 2: EDAX Spectrum of Pure and Cu Doped ZnO

Table 1. FTIR Functional Group of Pure and Cu Doped ZnO

S. No.	Sample Name	Wave Number (cm^{-1})				
		O=H stretching Vibration	C=H Stretching Vibration	H=O=H Stretching vibration	C=HO Stretching Vibration	Zn=O Stretching Vibration
1.	Pure ZnO	3733.72	2298.72	1689.26	1153.69	559.46
2.	Cu doped ZnO	3882.70	2353.15	1724.36	1170.79	557.42

Table 2. EDAX Spectrum of Pure and Cu Doped ZnO

Sample	Element	App Conc	Intensity Corrn	Weight%	Weight% Sigma	Atomic%
Cu doped ZnO	O K	28.02	1.1911	31.98	0.66	65.59
	Cu K	4.88	0.9111	7.28	0.47	3.77
	Zn K	40.72	0.9114	60.74	0.72	30.54
Pure ZnO	O K	21.88	1.1241	26.42	0.69	59.46
	Zn K	50.17	0.9258	73.58	0.69	40.54

4.3 XRD

The XRD pattern of prepared Pure ZnO and Cu doped ZnO were shown in fig. 3. The prepared sample confirms the presence of a hexagonal structure. The diffraction peaks of the prepared Pure ZnO at 2θ =36.44, 63.03, 68.1 and 69.29 then the diffraction peaks of Cu doped ZnO at 2θ=36.29, 62.89, 67.98 and 69.07 are identified. Both are corresponding to the hkl planes are (101), (103), (112) and (201). The average crystalline size (D) of Pure ZnO and Cu doped ZnO was 18.67 and 16.25nm. Thus the average crystalline size of Pure ZnO is higher than the Cu doped ZnO due to the capping of Copper. The unit cell volume (V), lattice parameters a and c decreased due to an increase in crystalline size, and it was shown in table 3.

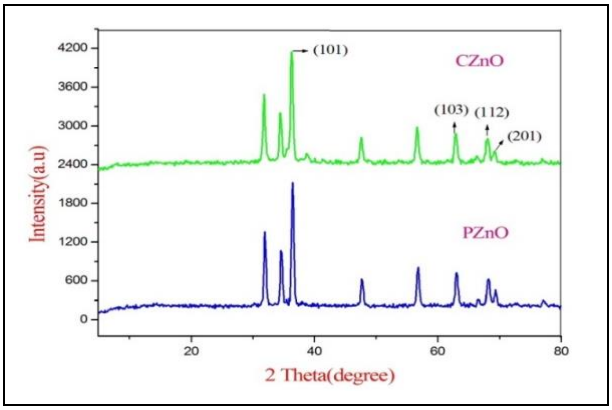

Fig. 3: XRD Pattern for Pure and Cu Doped ZnO

4.4 SEM Analysis

The morphological structure of the prepared nanocomposites was revealed in SEM. The synthesized micrographs of pure and Cu doped ZnO nanoparticles were crystalline. Fig 4. pure ZnO (a & b) and fig. 5. Cu doped ZnO (c & d) both show the needle shape nanostructure. The particle size of the pure ZnO was 25.45nm to 103.36nm in diameter, and Cu doped ZnO was 25.71 nm to 74.97nm in diameter.

4.5 UV-Vis Analysis

UV-Vis spectra of pure ZnO and Cu doped ZnO nanoparticles are shown in Fig. 6. The spectrum was recorded in the range of 200-750nm. Samples are exhibits the absorbance peak in the UV region. The presence of maximum absorbance peak around 356 nm in pure and Cu doped ZnO samples.

Table 3. SEM spectrum of pure and Cu doped ZnO

Sample Name	2theta (deg)	FWHM (deg)	D (Å)	Intensity (Counts)	Crystalline size (nm)	Average Crystalline size (nm)	hkl	Lattice Constant		Unit Cell Volume (V)
								a=b	c	
PZnO	36.44	0.4703	2.46	1195	17.78	18.67	101	3.22	5.20	47.71
	63.03	0.5020	1.47	358	18.56		103			47.53
	68.12	0.5205	1.37	292	18.42		112			46.41
	69.29	0.4849	1.35	163	19.91		201			46.80
CZnO	36.29	0.5015	2.47	1104	16.67	16.25	101	3.23	5.18	47.18
	62.89	0.5500	1.47	326	16.93		103			46.87
	67.98	0.6090	1.37	267	15.73		112			46.77
	69.07	0.6159	1.35	123	15.66		201			47.04

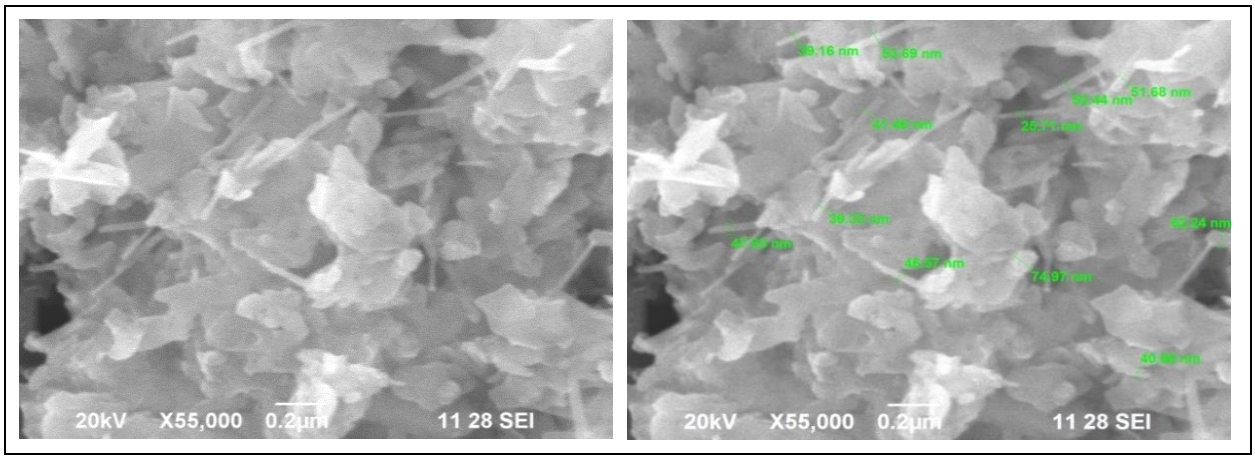

Fig. 4: SEM Analysis for Pure ZnO

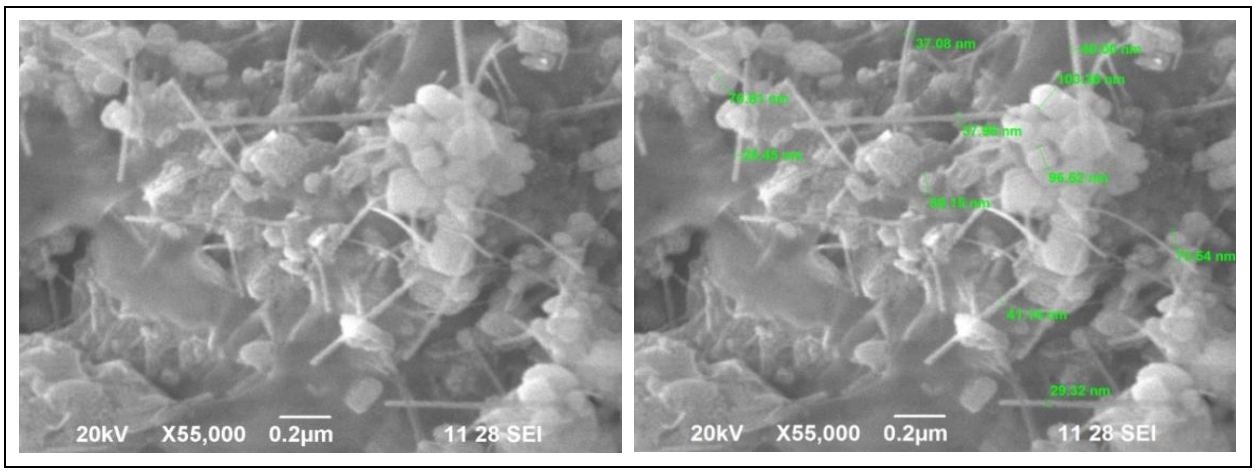

Fig. 5: SEM Analysis for Pure and Cu Doped ZnO

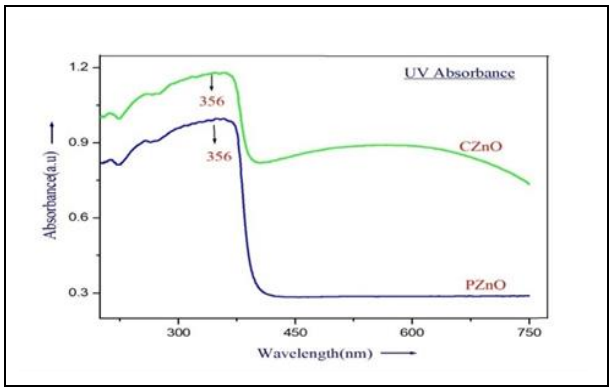

Fig. 6: UV-Vis Spectrum of Pure and Cu Doped ZnO

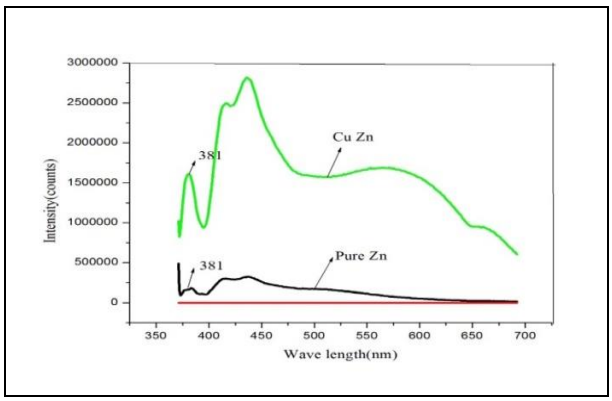

Fig 4.7: PL Analysis

Table 4.4: UV-Vis spectrum of pure and Cu doped ZnO

S. No.	Sample Name	Wave Length nm)	Band Gap Energy (eV)
1.	PZnO	356	3.42
2.	CZnO	356	3.42

4.6 PL Analysis

Photoluminescence spectroscopy was used to measure the intensity of emission radiations. Figure 4.7 depicts the emission radiation of pure and Cu doped ZnO. For both pure and Cu doped ZnO, the excitation wavelength is in the 378nm band. Pure ZnO has a normal bandgap energy of 3.31 eV, while the measured bandgap energy of both samples is 3.42 eV.

5. CONCLUSION

In this work, the zinc oxide nanoparticles were synthesized by using with and without doping agent copper sulphate. The samples were characterized by FTIR, EDAX, XRD, SEM, UV and PL.

- The FTIR analyses show the different functional groups are present in the given samples of pure and Cu doped ZnO nanoparticles.
- EDX proves the chemical elements are present in the prepared samples. The pure and Cu doped Zinc Oxide nanoparticles are having Zinc (Zn) Oxide (O) and Copper (Cu).
- XRD pattern confirms the presence of hexagonal structure, and it is used to determine the crystalline size of the sample and unit cell dimensions of the prepared sample Pure and Cu doped ZnO.
- SEM shows the morphological structure of the prepared sample. Moreover, its gives the Needle shapes for the pure ZnO and Cu doped ZnO, so the SEM proves that the doping agent can same morphological structure of the given sample.
- UV-Vis spectrum shows the bandgap energy and wavelength for Pure and Cu doped ZnO. The bandgap energy of Pure and Cu doped ZnO was 3.42eV.

- PL analysis reveals the bandgap energy and optical absorption of the sample.

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